

Viscous flow and thermal characteristics of N-Amyl alcohol

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Abstract

Based on experimental values of dynamic viscosity and density of n-amyl alcohol in the pressure range of 11.09 MPa – 49.14 MPa and temperature range of 288.95 K – 567.35 K the activation Gibbs energy of viscous flow, the activation enthalpy of viscous flow, the activation entropy of viscous flow, the isobaric expansion coefficient and the isothermal compression coefficient were calculated and the changes of these parameters depending on temperature and pressure were analyzed. It was determined that with the increase in temperature at a given pressure, the activation Gibbs energy of viscous flow first decreases and then increases, the activation enthalpy of viscous flow and the activation of entropy of viscous flow only decrease, and the isobaric expansion coefficient and isothermal compression coefficient only increase. The obtained results show that the isobars in the dependences of $\Delta H_{\eta}^{\ddagger} = f(T)_p$, $\Delta S_{\eta}^{\ddagger} = f(T)_p$, $\alpha_p = f(T)_p$ and $\beta_T = f(T)_p$ they intersect at a point. Accordingly, it becomes $T_i(\Delta H_{\eta}^{\ddagger}) \approx 385$ K, $T_i(\Delta S_{\eta}^{\ddagger}) \approx 325$ K, $T_i(\alpha_p) \approx 282$ K and $T_i(\beta_T) \approx 282$ K.

Keywords: n-amyl alcohol, viscosity, density, activation parameters of viscous flow, isobaric expansion coefficient, isothermal compression coefficient.

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1. Introduction

N-amyl alcohol or 1-pentanol ($C_5H_{11}OH$) is a saturated diatomic alcohol and 8 isomers are known [1, 2, 3, 4]. Under normal conditions, it is a colorless liquid with

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an unpleasant odor. N-Amyl alcohol is obtained by distillation from castor oils and petroleum cracking gases and has all properties related to alcohols (forms alcoholates with alkali metals, forms ethers with inorganic and organic acids, etc.). N-Amyl alcohol is used as a solvent for various oils, resins and waxes, and as an extractant for uranium and niobium salts [1, 2]. N-Amyl alcohol is easily soluble in water, its molar mass is 88.15 g/mol , freezing temperature is -78°C and boiling temperature is 138°C at normal atmospheric pressure. N-Amyl alcohol is toxic, its vapor can irritate the skin and eyes, it is also explosive and fire hazard. Complex esters of N-Amyl alcohol are used as solvents, plasticizers for polyvinyl chloride and acetyl cellulose, aromatic substances in perfumery [1, 3, 5].

In this work, the viscous flow and thermal characteristics of n-amyl alcohol in a wide range of pressure (p) and temperature (T) were studied. For this purpose, based on the experimental values of dynamic viscosity (η) and density (ρ) of n-amyl alcohol in the pressure range of $1.09 \text{ MPa} - 49.14 \text{ MPa}$ and temperature range of $288.95 \text{ K} - 567.35 \text{ K}$ [4] activation Gibbs energy of viscous flow (ΔG_η^\ddagger), activation enthalpy of viscous flow (ΔH_η^\ddagger), activation entropy of viscous flow (ΔS_η^\ddagger), isobaric expansion coefficient (α_p) and isothermal compression coefficient (β_T) at the considered pressures and temperatures) were determined and based on them, the structural features of the considered liquid were analyzed.

2. Method of calculation

By analyzing the changes in the activation parameters (ΔG_η^\ddagger , ΔH_η^\ddagger , ΔS_η^\ddagger) of the viscous flow of liquids under the influence of various external factors (temperature, pressure, etc.), it is possible to obtain certain information about the structural characteristics and existing interactions in liquids [6, 7]. According to Frenkel and Eyring's theories of viscous flow of fluids [8, 9], activation Gibbs energy of viscous flow (ΔG_η^\ddagger),

$$\Delta G_\eta^\ddagger = RT \ln \frac{\eta}{\eta_0} \quad (1)$$

is defined by the expression According to Eyring's theory, $\eta_0 = N_A h \rho / M$ [8, 9]. Here, R is the universal gas constant, N_A is Avogadro's number, h is Planck's constant, and M is the molar mass of the liquid. Dynamic viscosity (η) and density (ρ) of liquid at absolute temperature T are determined experimentally.

Activation enthalpy of viscous flow (ΔH_η^\ddagger)

$$\Delta H_\eta^\ddagger = R \frac{\partial \ln(\eta/\eta_0)}{\partial (1/T)} \quad (2)$$

can be determined by the expression [9, 10]. After determining ΔG_η^\ddagger from expression (1) and ΔH_η^\ddagger from expression (2).

$$\Delta G_{\eta}^{\ddagger} = \Delta H_{\eta}^{\ddagger} - T\Delta S_{\eta}^{\ddagger} \quad (3)$$

according to the expression [9], we can determine the activation entropy of the viscous flow ($\Delta S_{\eta}^{\ddagger}$).

The study of thermal properties of liquids (isobaric expansion coefficient, isothermal compression coefficient, adiabatic compression coefficient, etc.) is very important for the description of various processes [5, 11, 12]. These properties also play an important role in providing various models for determining the molecular structure and macroscopic properties of liquids. The study of the thermal properties of liquids, especially the coefficient of isobaric expansion and the coefficient of isothermal compression, allows to clarify the essence of molecular interactions between molecules in liquids. The study of thermal properties of liquids is also very important in the description of structural characteristics that occur in liquids [5, 13, 14, 15]. It is known from thermodynamics that the isobaric expansion coefficient (α_p) and the isothermal compression coefficient (β_T) of liquids are

$$\alpha_p = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_p \quad (4)$$

$$\beta_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial p} \right)_T \quad (5)$$

we can define with expressions [9, 13].

3. Experiment

Object of study and methods. n-amyl alcohol was taken as the research object. The dynamic viscosity and density of N-amyl alcohol in a wide range of temperature (288.95 K – 567.35 K) and pressure (1.09 MPa – 49.14 MPa) were studied. Dynamic viscosity (η) and density (ρ) of N-amyl alcohol at different temperatures and pressures were measured by viscometry and densitometry methods. Experimental values of dynamic viscosity and density of N-amyl alcohol at different temperatures and pressures are taken from [4].

4. Results and discussion

Temperature dependences of various isobars of N-amyl alcohol viscous flow activation parameters ($\Delta G_{\eta}^{\ddagger}$, $\Delta H_{\eta}^{\ddagger}$, $\Delta S_{\eta}^{\ddagger}$) are shown in Figures 1-3. Let's note that the activation Gibbs energy ($\Delta G_{\eta}^{\ddagger}$) of viscous flow is the energy required for 1 mole of liquid molecules to flow at a given pressure and temperature. Activation enthalpy of viscous flow ($\Delta H_{\eta}^{\ddagger}$) characterizes the changes occurring in the solution in terms of energy. Thus, the large value of $\Delta H_{\eta}^{\ddagger}$ 1 indicates that the considered system has a

stronger structure. The activation entropy of the viscous flow ($\Delta S_{\eta}^{\ddagger}$) provides valuable information about the structural changes occurring in the liquid. A large value of $\Delta S_{\eta}^{\ddagger}$ for the considered system indicates that the system is more structured [12, 16, 17].

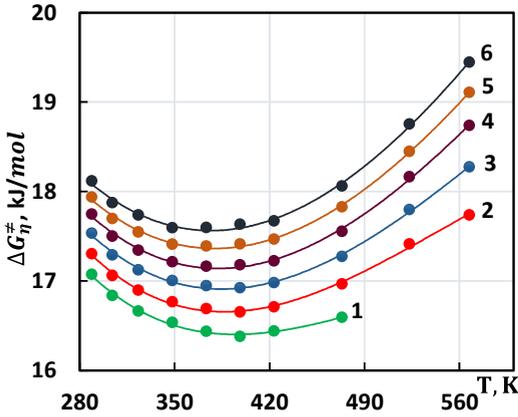


Figure 1. Temperature dependence of activation Gibbs energy of viscous flow of N-amyl alcohol at different pressures

- 1 – 1.09 MPa,
- 2 – 9.91 MPa,
- 3 – 19.72 MPa,
- 4 – 29.53 MPa,
- 5 – 39.33 MPa,
- 6 – 49.14 MPa

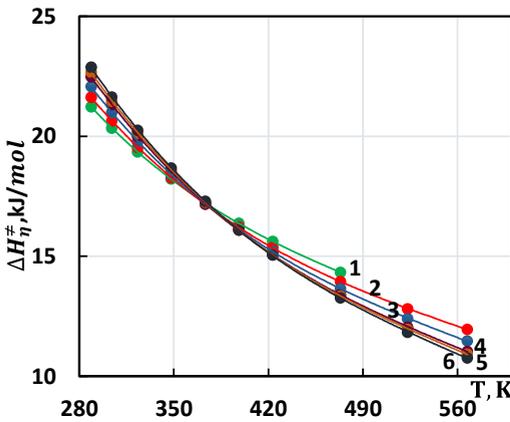


Figure 2. Temperature dependence of activation enthalpy of viscous flow of N-amyl alcohol at different pressures

- 1 – 1.09 MPa,
- 2 – 9.91 MPa,
- 3 – 19.72 MPa,
- 4 – 29.53 MPa,
- 5 – 39.33 MPa,
- 6 – 49.14 MPa

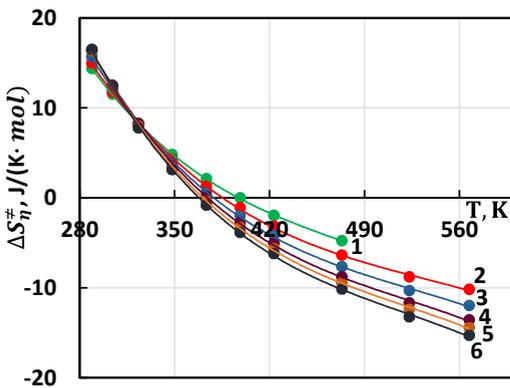


Figure 3. Temperature dependence of the activation entropy of viscous flow of N-amyl alcohol at different pressures:

- 1 – 1.09 MPa,
- 2 – 9.91 MPa,
- 3 – 19.72 MPa,
- 4 – 29.53 MPa,
- 5 – 39.33 MPa,
- 6 – 49.14 MPa.

It can be seen from Figure 1 that the value of the function $\Delta G_{\eta}^{\ddagger} = f(p)_T$ which characterizes each isotherm, increases with increasing pressure for n-amyl alcohol. As the temperature increases, the value of the function $\Delta G_{\eta}^{\ddagger} = f(T)_p$ characterizing each isobar first decreases and then increases. The coordinates of the minimum observed point $(T_{min}; \Delta G_{\eta}^{\ddagger}(T_{min}))$ as the pressure increases, the T_{min} point shifts to lower temperatures, and the value of the $\Delta G_{\eta}^{\ddagger}(T_{min})$ point increases. It can be seen from Figure 2 that $\Delta H_{\eta}^{\ddagger}$ decreases as the temperature increases for each isobar, and the lines characterizing each isobar intersect at one point in the dependence of $\Delta H_{\eta}^{\ddagger} = f(T)_p$. So, at the intersection point $\Delta H_{\eta}^{\ddagger} = f(T)_p$. The coordinates of this point for N-amino alcohol correspond to the values $T_i(\Delta H_{\eta}^{\ddagger}) \approx 385 K$, $\Delta H_{\eta}^{\ddagger}(T_i) \approx 16.7 kJ$. It can be seen from Figure 3 that $\Delta S_{\eta}^{\ddagger}$ decreases as the temperature increases for each isobar, and the lines characterizing each isobar intersect at one point in the dependence of $\Delta S_{\eta}^{\ddagger} = f(T)_p$. As it can be seen, the regularities observed in the dependence $\Delta H_{\eta}^{\ddagger} = f(T)_p$ are also observed to some extent in the dependence $\Delta S_{\eta}^{\ddagger} = f(T)_p$. However, in the observed case, $\Delta H_{\eta}^{\ddagger} > 0$ is always, and after a certain temperature value, $\Delta S_{\eta}^{\ddagger} < 0$. Let's note that $\Delta S_{\eta}^{\ddagger}$ takes negative values in dependence of $\Delta G_{\eta}^{\ddagger} = f(T)_p$ at temperatures higher than the minimum observed temperature T_{min} , and at temperature T_{min} it becomes $\Delta S_{\eta}^{\ddagger}(T_{min}) = 0$. This result is understandable. Because it is known from thermodynamics that $\Delta S_{\eta}^{\ddagger} = -(\partial \Delta G_{\eta}^{\ddagger} / \partial T)_p$ [9]. It can also be seen from Figure 3 that the coordinate of the lines characterizing each isobar in the dependence of $\Delta S_{\eta}^{\ddagger} = f(T)_p$ for the studied liquid $T_i(\Delta S_{\eta}^{\ddagger}) \approx 325 K$ and $\Delta S_{\eta}^{\ddagger}(T_i) \approx 7.9 J/mole$. They intersect at $\approx 7.9 J/mole$. That is, $(\partial \Delta S_{\eta}^{\ddagger} / \partial p)_T \approx 0$ for n-amyl alcohol at a temperature of 325 K.

Temperature dependences of different isobars of isobar expansion (α_p) and isothermal compression (β_T) coefficients of N-amyl alcohol are shown in figures 5 and 6.

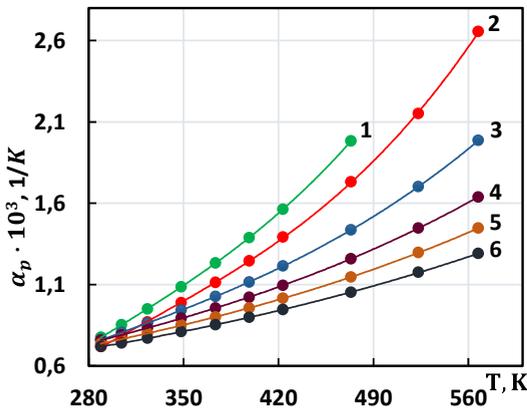


Figure 4. Temperature dependence of the isobaric expansion coefficient of N-amyl alcohol at different pressures.

- 1 – 1.09 MPa,
- 2 – 9.91 MPa,
- 3 – 19.72 MPa,
- 4 – 29.53 MPa,
- 5 – 39.33 MPa,
- 6 – 49.14 MPa.

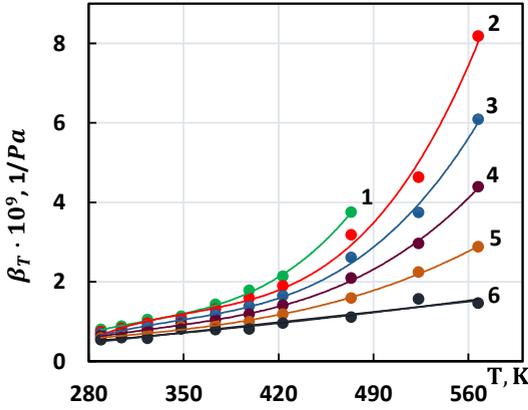


Figure 5. Temperature dependence of the isothermal compression coefficient of N-amyl alcohol at different pressures.

- 1 – 1.09 MPa,
- 2 – 9.91 MPa,
- 3 – 19.72 MPa,
- 4 – 29.53 MPa,
- 5 – 39.33 MPa,
- 6 – 49.14 MPa.

It can be seen from Figures 4 and 5 that the values of functions $\alpha_p = f(p)_T$ and $\beta_T = f(p)_T$, which characterize each isotherm, increase with increasing pressure for n-amyl alcohol. Also, the values of functions $\alpha_p = f(p)_T$ and $\beta_T = f(p)_T$, which characterize each isobar, also increase with the increase in temperature. The obtained results show that, as in the dependences $\Delta H_\eta^\ddagger = f(T)_p$ and $\Delta S_\eta^\ddagger = f(T)_p$ in n-amyl alcohol, both $\alpha_p = f(T)_p$ and $\beta_T = f(T)_p$ has a temperature value such that at this temperature $(\partial\alpha_p/\partial p)_T \approx 0$ and $(\partial\beta_T/\partial p)_T \approx 0$. As a result of our research, it was determined that this temperature value is $T_i(\alpha_p) \approx 282\text{ K}$ and $T_i(\beta_T) \approx 282\text{ K}$. In addition, at these temperatures $\alpha_p(T_i) \approx 0.73 \cdot 10^{-3}\text{ 1/K}$ and $\beta_T(T_i) \approx 0.6 \cdot 10^{-9}\text{ 1/Pa}$. It can be assumed that the inversion observed in the temperature dependences of the activation parameters of the viscous flow of n-amyl alcohol in the liquid phase, the isobar expansion and isothermal compression coefficients of different isobars is related to the various structural changes that occur in the liquid.

5. Conclusion

The temperature dependences of the viscous flow (ΔG_η^\ddagger , ΔH_η^\ddagger , ΔS_η^\ddagger) and thermal characteristics (α_p , β_T) of N-amyl alcohol at a pressure of 1.09 MPa – 49.14 MPa and a temperature range of 288.95 K – 567.35 K were analyzed. It was determined that with the increase in temperature, the value of the function $\Delta G_\eta^\ddagger = f(T)_p$, which characterizes each isobar, first decreases and then increases, and the temperature T_{min} corresponding to the minimum observed point shifts to lower temperatures. In the dependences $\Delta H_\eta^\ddagger = f(T)_p$ and $\Delta S_\eta^\ddagger = f(T)_p$, as the temperature increases for each isobar, the values of the quantities ΔH_η^\ddagger and ΔS_η^\ddagger decrease, and also $\Delta H_\eta^\ddagger = f(T)_p$ and $\Delta S_\eta^\ddagger = f(T)_p$ dependences, the isobars inter-

sect at one point and $T_i(\Delta H_\eta^\ddagger) \approx 385 \text{ K}$, $T_i(\Delta S_\eta^\ddagger) \approx 325 \text{ K}$, respectively. In the dependences $\alpha_p = f(T)_p$ and $\beta_T = f(T)_p$, as the temperature increases for each isobar, the values of the quantities α_p and β_T increase, as well as $\alpha_p = f(T)_p$ and $\beta_T = f(T)_p$ dependences, the isobars intersect at one point and $T_i(\alpha_p) \approx 282 \text{ K}$, $T_i(\beta_T) \approx 282 \text{ K}$ respectively.

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